



(MURI 09) SEARCH FOR NEW SUPERCONDUCTORS FOR ENERGY AND POWER APPLICATIONS

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Final Report

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ABSTRACT

The search for new materials with interesting properties is probably the most challenging problem in modern condensed matter and materials physics. Important developments in the physics of condensed matter usually start with the discovery of an interesting phenomenon and it is probably safe to state that “without the material there is no physics”. This extends to many interesting phenomena including magnetism, ferroelectricity, superionicity etc. Perhaps one of the most intensely explored phenomena, superconductivity, relied mostly on the almost accidental discoveries of new superconductors. The SuperSearch for New Superconductors MURI project departs from this motivated by the BAA # 13 on “Search for New Superconductors for Energy and Power Applications”. We developed a novel methodology for an enlightened search for new materials, using a combination of Synthesis and Screening techniques. While no single approach can assure the discovery of new classes of superconductors, our proposal established a rational methodology for the search for new superconductors.

We developed the methodology described in the original proposal, we have discovered a large number of new superconductors, have provided a search service to many researchers world wide, and continue the search in many new systems.

EXECUTIVE SUMMARY

The results obtained during this project include: development of unique instrumentation which will continue producing first rate science, discovery of many superconducting systems which will continue to be investigated by the members of the MURI and others, education of many young scientists (undergraduate, graduate and postdoctoral), and many collaborations nationally and internationally. A most successful project.

I. ACCOMPLISHMENTS

This project is dedicated to the development of new search techniques and to implement an exhaustive search for new superconductors. This project is oriented very strongly towards the search and discovery of new materials. We developed an efficient combinatorial method that allows simultaneous search for many superconducting systems. This highly interdisciplinary project was implemented using the following crucial ingredients: 1) Synthesis by many preparation methods 2) fast, sensitive and efficient methods that allow discarding the uninteresting parts of the phase diagram and 3) a comprehensive battery of tests including transport, magnetization, specific heat, optical and microwave response.

During this project we have addressed all the aims of the proposal. Several major accomplishments include

1. **The Magnetic Field Modulated Microwave Spectroscopy (MFMMS)** was developed, provided extensive service to the various AFOSR MURIs working in this field and to others. The Magnetic Field Modulated Microwave Spectroscopy (MFMMS) system with its selectivity and unparalleled limit of detection of minority superconducting phases, of 10^{-12} cc³ embedded in a non-superconducting matrix, has become a powerful tool for the whole community. The discoveries already made, validate the search methodology and now large searches are underway. Samples were exchanged, and coordinated measurements were done between the different MURI partners and others elsewhere. More than 2100 samples have been measured to date.

2. **Joint searches** using arc-melting, powder metallurgy, sputtering, sol gel and thin film techniques in a variety of possible superconducting systems with potential for new discoveries. The search methodology described in the original proposal is being applied to a variety of bulk materials systems including: mixtures of well-known superconductors, borides, carbides, silicides, and chalcogenides. In addition, a number of thin film systems have been explored: A15s, superlattices, arrays of nanodots, and phase-spread alloys. See Table I below for a list of all the systems investigated so far.

3. **Unusual systems** investigated. Search for new superconductors is underway in the largest collection of micrometeorites available from Susan Taylor at the Army Core of Engineers and in a variety of meteorites, lunar and martian rocks in collaboration with Prof. M. Thiemens, Chemistry Department, UCSD. Conversations (at different stages) are underway with two museums to get access to their collection of meteorites.

4. **Theoretically driven search.** The overarching goal of this work is to identify the universal trends of unconventional superconductors that can be used for a directed search of new superconducting materials. We found earlier a universal scaling relationship between the superfluid density and the product of $T_c \times \Delta$ (Δ is the superconducting energy gap) in unconventional superconductors. We showed lately that this scaling is also present in organic superconductors. This now provides a theoretical framework for the directed search for new superconductors used by us and others.

5. **Collaborations** are underway in a variety of combinations with the other SuperSearch MURIs, individual researchers, Army Core of Engineers and science museums. For a comprehensive list see Table II.

6. **New superconducting systems** found. A substantial number of new materials systems were found which exhibit superconductivity at cryogenic temperatures. Improving the T_c of these systems is underway. See Table III below.

II. PRACTICAL RESULTS

The results were summarized in 38 papers in first-rate refereed journals, were part of 8 PhD theses, presented as invited and contributed talks at major meetings, and had a major influence on the education of graduate students and postdoctoral fellows.

This research has also been crucial in the education of several PhD students impacting 8 theses works in different ways. Several (19) postdoctoral fellows have contributed partially to the research outlined above and 7 visitors contributed, sometimes free of cost. It is important to highlight that much of the research being done under this project benefits from extensive collaborations with chemist, physicists and engineers at UCSD and other institutions, thus the young investigators are exposed to an important modality of collaborative research.

The graduate students and postdocs associated with this project that have finished their tenure, are employed in industry, national labs and academia. They are also developing independent research in related fields.

Archival Publications (published– project entirety)

1. [*Towards a Two-Dimensional Superconducting State of \$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4\$ in a Moderate External Magnetic Field*](#), A. Shafgans, A. LaForge, S. Dordevic, M. Qazilbash, W. Padilla, K. Burch, Z. Li, S. Komiya, Y. Ando, and D. Basov, Phys. Rev. Lett. **104**, 157002 (2010).
2. [*Superconductivity at 7.3K in \$\text{Ti}_2\text{InN}\$*](#) , A. Bartolozzo, G. Serrano, A. Serquis, D. Rodrigues Jr., C. A. M. dos Santos, Z. Fisk, A. Machado. Solid State Commun. **150**, 1364 (2010).
3. [*Breakdown of the Universal Josephson Relation in Spin-ordered Cuprate Superconductors*](#), A. A. Schafgans, C. C. Homes, G. D. Gu, Seiki Komiya, Yoichi Ando, and D. N. Basov, Phys. Rev. B **82**, 100505(R) (2010)
4. [*Methodology and Search for Superconductivity in the La-Si-C system*](#), J. de la Venta, A. Basaran, T. Grant, A. Machado, M. Suchomel, R. Weber, Z. Fisk, and Ivan K. Schuller, Supercond. Sci. Technol. **24**, 075017 (2011)
5. [*Manifesto for Higher \$T_c\$*](#) , D. Basov and A. Chubukov, Nature Physics **7**, 272 (2011)
6. [*Incoherent c-Axis Interplane Response of the Iron Chalcogenide \$\text{FeTe}_{0.55}\text{Se}_{0.45}\$ Superconductor from Infrared Spectroscopy*](#), S.J. Moon, C.C. Homes, A. Akrap, Z.J. Xu, J.S. Wen, Z.W. Lin, Q. Li, G.D. Gu, and D.N. Basov, Phys. Rev. Lett. **106**, 217001 (2011).
7. [*Evidence of a Precursor Superconducting Phase at Temperatures as High as 180 K in \$\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}\$ \(\$R = \text{Y, Gd, Eu}\$ \) Superconducting Crystals from Infrared Spectroscopy*](#), A. Dubroka, M. Rossle, K.W. Kim, V. K. Malik, D. Munzar, D. N. Basov, A.A. Schafgans, S. J. Moon, C. T. Lin, D. Haug, V. Hinkov, B. Keimer, Th. Wolf, J. G. Storey, J. L. Tallon, and C. Bernhard, Phys. Rev Lett. **106**, 047006 (2011).
8. [*Ultrahigh Vacuum Sample Mount for X-ray Photoelectron Spectroscopy up to very High Temperature 150-1400 K*](#), M.S. Williamsen, S.K. Ray, Y. Zou, J. Dudek, S. Sen, M. Bissen, L. Kretsch, V.R. Palkar, M.F. Onellion, and P. Guptasarma, J. Vac. Sci. Technol. A **29**, 031602 (2011).
9. [*Electrodynamics of Correlated Electron Materials*](#), D. N. Basov, Richard D. Averitt, Dirk van der Marel, Martin Dressel, and Kristjan Haule, Rev. Mod. Phys. **83**, 471 (2011).
10. [*Superconductivity in \$\text{Mo}_5\text{SiB}_2\$*](#) , A.J.S.Machado, A.M.S.Costa, C.A.Nunes, C.A.M.dos Santos, T.Grant and Z. Fisk, Solid State Comm. **151**,1455 (2011).

11. [*Superconductivity in \$\text{Th}_3\text{Ni}_5\text{C}_5\$*](#) , A.J.S.Machado, T.Grant and Z.Fisk, Supercond. Sci. Technol. **24**, 095007 (2011).
12. *Superconductivity to 11.5K in $\text{Th}_{2-x}\text{Sc}_x\text{NiC}_2$* , A.J.S.Machado, T.Grant and Z.Fisk (in preparation).
13. *Crystal Structure and Properties of $\text{Tb}(\text{Mn,Cu})\text{O}_3$* , S.K. Ray, M.S. Williamsen, S. Sen, Y. Zou, P. Guptasarma (in preparation).
14. *Properties of Superconducting La-Si-C* , S. Sen, S.K. Ray, J.A. Dudek, M.S. Williamsen, Y. Zou, and P. Guptasarma (in preparation).
15. *Search for Superconductivity in V-VI compounds*, S. Sen and P. Guptasarma (in preparation).
16. *Phase Spread Alloy Fabrication and Characterization*, M. Marsh, J. de la Venta, A. Barasan, D. N. Basov, S. Dietze, O. Shpyrko, I. K. Schuller (in preparation).
17. [*Insulator-to-metal transition and correlated metallic state of \$\text{V}_2\text{O}_3\$ investigated by optical spectroscopy*](#), M.K. Stewart, D. Brownstead, S. Wang, K.G. West, J.G. Ramirez, M.M. Qazilbash, N.B. Perkins, Ivan K. Schuller, D. Basov, Phys. Rev. B, **85**(20), 205113 (2012).
18. [*Electron Spin Resonance of the Intermetallic Antiferromagnet \$\text{EuIn}_2\text{As}_2\$*](#) , P.F.S. Rosa, C. Adriano, T.M. Garitezi, R.A. Ribeiro, Z. Fisk, P.G. Pagliuso, Phys. Rev. B, **89**(9), 094408 (2012).
19. [*\$\text{Th}_2\text{NiC}_2\$: A Low Density of States Superconductor*](#), A.J.S. Machado, T. Grant, Z. Fisk, Supercond. Sci. Technol., **25**(4), 045010 (2012).
20. [*Infrared Measurement of the Pseudogap of P-Doped and Co-Doped High-Temperature \$\text{BaFe}_2\text{As}_2\$ Superconductors*](#), S.J. Moon, A.A. Schafgans, S. Kasahara, T. Shibauchi, T. Terashima, Y. Matsuda, M. A. Tanatar, R. Prozorov, A. Thaler, P. C. Canfield, A.S. Sefat, D. Mandrus, and D.N. Basov, Phys. Rev. Lett. **109**, 027006 (2012).
21. [*Electronic Correlations and Unconventional Spectral Weight Transfer in the High-Temperature Pnictide \$\text{BaFe}_{2-x}\text{Co}_x\text{As}_2\$ Superconductor Using Infrared Spectroscopy*](#), A. A. Schafgans, S. J. Moon, B. C. Pursley, A. D. LaForge, M. M. Qazilbash, A. S. Sefat, D. Mandrus, K. Haule, G. Kotliar, and D. N. Basov, Phys. Rev. Lett. **108**, 147002 (2012).
22. [*Corrigendum: Methodology and Search for Superconductivity in the \$\text{La-Si-C}\$ System*](#), J. de la Venta, Ali C. Basaran, T. Grant, A.J.S. Machado, M.R. Suchomel, R.T. Weber, Z. Fisk and Ivan K. Schuller, Supercond. Sci. Technol. **25**, 049501 (2012).
23. [*Magnetism and the Absence of Superconductivity in the Praseodymium-Silicon System Doped with Carbon and Boron*](#), J. de la Venta, A.C. Basaran, T. Grant, J.M. Gallardo-Amores, J.G. Ramirez, M.A. Alario-Franco, Z. Fisk, I.K. Schuller, J. Magn. Magn. Mater., **340**, 27 (2013).
24. [*Ferromagnetism in Partially Oxidized \$\text{CuCl}\$*](#) , T. Sauerbeck, J. Pereiro, J.Wampler, J. Stanley, J. Wingert, O.G. Shpyrko, and Ivan K. Schuller, J. Magn. Magn. Mater., **346**, 161 (2013).
25. [*Sharp Raman Anomalies and Broken Adiabaticity at a Pressure Induced Transition from Band to Topological Insulator in \$\text{Sb}_2\text{Se}_3\$*](#) , A. Bera, L. Pal, D.V. Muthu, S. Sen, P. Guptasarma, U.V. Waghmare, A.K. Sood, Phys. Rev. Lett., **110**, 107401 (2013).

26. [*Electron Spin Resonance of the Intermetallic Antiferromagnet \$\text{EuIn}_2\text{As}_2\$*](#) , P.F.S. Rosa, C. Adriano, T.M. Garitezi, R.A. Ribeiro, Z. Fisk, P.G. Pagliuso, Phys. Rev. B, 89(9), 094408 (2012).
27. [*Evolution of \$\text{Eu}^{2+}\$ Spin Dynamics in \$\text{Ba}_{1-x}\text{Eu}_x\text{Fe}_2\text{As}_2\$*](#) , P.F.S. Rosa, C. Adriano, W. Iwamoto, T.M. Garitezi, T. Grant, Z. Fisk, P.G. Pagliuso, Phys. Rev. B., **88**(15), 159907 (2013).
28. [*Critical Current Density and Flux Pinning in \$\text{Zr}_{0.96}\text{V}_{0.04}\text{B}_2\$ Superconductor with \$\text{AlB}_2\$ Structure*](#), Soon-Gil Jung, J. Vanacken, V.V. Moshchalkov, S.T. Renosto, C.A.M. dos Santos, A.J.S. Machado, Z. Fisk, J. Albino Aguiar, J. Appl. Phys., **114**(13), 133905 (2013).
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30. [*Do Organic and other Exotic Superconductors Fail Universal Scaling Relations?*](#) S.V. Dordevic, D.N. Basov & C.C. Homes, Nature – Scientific Reports **3**, 1713 (2013).
31. [*Interlayer Coherence and Superconducting Condensate in the c-Axis Response of Optimally Doped \$\text{Ba}\(\text{Fe}_{1-x}\text{Co}_x\)_2\text{As}_2\$ High-Tc Superconductor Using Infrared Spectroscopy*](#), S.J. Moon, A.A. Schafgans, M.A. Tanatar, R. Prozorov, A. Thaler, P.C. Canfield, A.S. Sefat, D. Mandrus, and D.N. Basov, Phys. Rev. Lett. **110**, 097003 (2013).
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33. [*Superconductivity in Non-centrosymmetric \$\text{ThCoC}_2\$*](#) , T. Grant, A.J.S. Machado, D.J. Kim and Z. Fisk, Supercon. Sci. Technol., **27**, 035004 (2014).
34. [*Field-enhanced Magnetic Moment in Ellipsoidal Nano-hematite*](#), V. Malik, S. Sen, D.R. Gelting, M. Gajdardziska-Josifovska, M. Schmidt, P. Guptasarma, Mater. Res. Express **1** (2014) 026114.
35. [*Search for Superconductivity in \$\text{Fe}_{1+d}\text{Te}\$: Role of Oxidation State*](#), D. R. Gelting, N. P. Smith, S. Sen, M. Schofeld, A. Basaran, I. K. Schuller, M. Gajdardziska-Josifovska, P. Guptasarma, to be communicated Phys. Rev. B, available as preprint (2014).
36. [*Infrared Pseudogap in Cuprate and Pnictide High-temperature Superconductors*](#), S. J. Moon, Yunsang Lee, A.A. Schafgans, A.V. Chubukov, S. Kasahara, T. Shibauchi, T. Terashima, Y. Matsuda, M.A. Tanatar, R. Prozorov, A. Thaler, P.C. Canfield, A.S. Sefat, D. Mandrus, K. Segawa, Y. Ando, and D. N. Basov, Phys. Rev. B. **90**, 014503 (2014).
37. [*Near-field Techniques for Probing Collective Modes of Anisotropic Superconducting Thin Films*](#), H. T. Stinson, J.S. Wu, B.Y. Jiang, Z. Fei, A.S. Rodin, B. Chapler, A.S. Mcleod, A. Castro Neto, Y.S. Lee, M. M. Fogler, and D.N. Basov (Under review in PRB).
38. [*Search for Superconductivity in Extraterrestrial Materials: A Most Unusual Fishing Expedition*](#), S. Guenon, J. G. Ramirez, Ali C. Basaran, M. Thiemens, S. Taylor, and Ivan K. Schuller (under review Scientific Reports)

Changes in research objectives, if any: None

Change in AFOSR program manager, if any: None

Extensions granted or milestones slipped, if any: None

Include any new discoveries, inventions, or patent disclosures during this reporting period (if none, report none):

Table I: Systems explored (superconductors and non-superconductors).

OXIDES	CALCOGENIDES	SILICIDES	OTHERS
MoSrEuCuO	Bi ₂ Te ₃	Eu-Si	FePc (Phthalocyanine)
GdBa ₂ Cu ₃ O _x	FeTe _{0.65} Se _{0.35}	LaFe ₂ Si ₂	H ₂ O treated Graphite
SmBa ₂ Cu ₃ O _x	FeSe:K	Eu-Si-Nb	HOPG (Graphene)
MnO	FeTe	Cu ₃ Si	Teflon
V ₂ O ₃	Bi ₂ Te ₃ Cu _x	CARBIDES	Irradiated Si
Pb-Mo-Cl-O	Bi ₂ Se ₃ Cu _x	Pr-Si-C	Nb ₃ Ge
YBa ₂ Cu ₃ O ₇	Bi ₂ Se ₃	Eu-Si-C	ErRh ₄ B ₄
Bi ₂ Sr ₂ CaCu ₂ O ₈ (UD, OD)	Sb ₂ Se ₃	V-Si-C	(Ga,Mn)As
CuO	ZrSe ₂	Sm-Si-C	Hf(FeCo)P
Y _{1-x} Ca _x CrO ₃	Fe-Te-Se	BORIDES	Hf-Fe-C-P
YCrO ₃	Cu-Se-V	Eu ₅ Si ₃ B	
Fe ₃ O ₄	CHLORIDES	MgB ₂	
SiO ₂	FeCl ₂	TiB ₂	
La-Fe-Ba-Bi-O	CuCl/Si	AlB ₂	
V ₂ O ₅ :Ti	CuCl	TiB ₂	
CaCuO ₂ /SrTiO ₃	CuCl ₂	Eu ₅ Si ₃ B	
(Mo/Cu)Sr ₂ ReCu ₂ O _x , RE: (Y, Er & Tm)	Cu-Se-Cl	TiB ₂	

Table II: Worldwide service and collaborations.

Collaborator	Institution
M. A. Alario-Franco	Universidad Complutense de Madrid, Spain
M. Aronson	Stony Brook University, USA
M. R. Beasley	Stanford University, USA
D. Esquinazi	Universität Leipzig, Germany
I. Felner	Jerusalem, Israel
T. J. Haugan	The Air Force Research Lab., USA
J. Hirsch	University of California – San Diego, USA
G. Larkin	Florida International University, USA
B. Maple	University of California – San Diego, USA
S. Risbud	University of California – Davis, USA
J. Sonier	Simon Fraser University, Canada
S. Taylor	Cold Regions Lab., USA
M. Thiemens	University of California – San Diego, USA
R. Puzniak	Institute of Physics, Warsaw, Poland

Table III New superconductors, discovered by UCSD MURI team.

BORIDES	T_c (K)
Nb _{0.9} Zr _{0.1} B	11.2
ZrNb _x B	9.0
ZrV _x B	9.0
ThNi ₂ Si ₂ B _x	8.5
Th(RE)B ₄ (3 compounds)	5.8
Zr _{0.98} Ni _{0.2} B ₂	5.7
Mo ₅ Si ₂ B (7 compounds)	5.5
Zr _{0.99} Ta _{0.01} B ₂	5.5
Nb _{0.9} Ni _{0.1} B ₂	5.3
Zr _{0.99} Nb _{0.01} B ₂	5.2
Zr _{0.91} Pt _{0.09} B ₂	3.7
W ₂ NiB ₂	3.5
ThMoB ₄	2.8
CALCOGENIDES	
ZrCu _x Te _{1.5}	10.0
ZrV _x S ₂	7.0 – 9.0
ZrV _x Se ₂	7.0 – 9.0
ZrV _x Te	7.0 – 9.0
CARBIDES	
ThCo _{0.6} Ni _{0.4} C ₂	12.0
Th _{2-x} Sc _x NiC ₂	9.0– 11.0
Th ₂ NiC ₂	8.5
Sc ₃ CoC ₄	7.0
ThNi ₄ C	5.1
Th ₃ Ni ₅ C ₅	5.0
Th ₅ Ni ₄ C	5.0
ThCoC ₂	2.7
ThNiC ₂	2.7
YCoC ₂	2.5
OTHERS	
Zr ₂ CuSb ₃	8.8
ZrVGe	6.0
HfV ₂ Ga ₄	4.0
Y ₃ NiCSi ₂	3.8
ThSiGe	3.4
Y ₅ Ni ₂ Bi	3.3
CaCeIr	3.0